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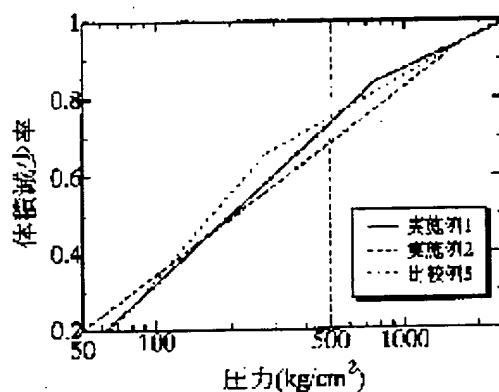
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(54) POSITIVE ELECTRODE ACTIVE MATERIAL FOR NON-AQUEOUS SECONDARY BATTERY, POSITIVE ELECTRODE AND SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve the load characteristic of a battery without hindering the active material filling performance into a positive electrode.

SOLUTION: This positive electrode active material is obtained by adjusting the primary grains of the Li compound oxide mainly composed of at least one kind or more of CO, Ni, Mn and Li to the porous secondary grains through each process of calcination, pulverization and dispersion, spray, granulation and burning. The positive electrode active material having 0.1-1 μm of pore mean diameter with the pore distribution measurement by the mercury press-in method and 0.01 cm^3/g or more of total volume of the pores having a diameter at 0.01-1 μm is used. Furthermore, as the secondary grains, the spherical secondary grains having 4-20 μm of mean grain diameter, 1.8 g/cm^2 or more of tap



density, 500 kg/cm^2 or more of inflection point of the volume reduction rate by the Cooper plot method is desirable.

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CLAIMS

[Claim(s)]

[Claim 1] Co, nickel, and Mn Positive active material for nonaqueous rechargeable batteries characterized by the sum total of the volume of pore with the path which it is the particle of the porosity which consists of a lithium multiple oxide which uses as a principal component one or more sorts of elements chosen from a group and a lithium, and the pore pitch diameter in the pore distribution measurement by the method of mercury penetration is within the limits which is 0.1-1 micrometer, and is 0.01 to 1 micrometer consisting of a particle which is more than 0.01cm³/g.

[Claim 2] The positive electrode for nonaqueous rechargeable batteries characterized by using positive active material according to claim 1.

[Claim 3] The positive electrode for nonaqueous rechargeable batteries with which positive active material is characterized by being the lithium multiple oxide in which insertion and desorption are possible reversibly, and holding the lithium ion in the arborescence network of carbon system electric conduction material as a porous aggregated particle lump with which the above-mentioned positive active material is a particle according to claim 1 in the positive electrode with which the mixture of this positive active material, carbon system electric conduction material, and a binder was formed in the shape of film on the charge collector, and primary particles gathered.

[Claim 4] The nonaqueous rechargeable battery characterized by using positive active material according to claim 1.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to amelioration of the rechargeable battery which used the positive active material, the positive electrode, and the above-mentioned positive active material for nonaqueous rechargeable batteries.

[0002]

[Description of the Prior Art] In recent years, the formation of small high performance and cordless-izing of an electronics device progress, and interests have gathered for the rechargeable battery as a drive power source for these pocket devices. The nonaqueous rechargeable battery represented by especially the rechargeable lithium-ion battery has great expectation as a cell which has a high voltage and a high energy consistency. The multiple oxide (it is hereafter described as a lithium multiple oxide) which makes a subject lithiums, such as the compound 2 which can carry out insertion desorption of the lithium ion reversibly, for example, LiCoO_2 , and LiNiO_2 , and transition metals as positive active material used for a nonaqueous rechargeable battery is typical. Although there is above LiCoO_2 as positive active material for lithium secondary batteries already put in practical use among such lithium multiple oxides, this LiCoO_2 is an expensive ingredient from there being no improvement room of an energy density, and using cobalt rare in resource, and expensive. Therefore, LiNiO_2 as alternate material which can obtain a high energy consistency, and manganese cheap and abundant in resource were used. Ingredient development of LiMn_2O_4 grade is also performed energetically.

[0003] Although these lithium multiple oxides have electronic conduction nature comparatively high as an oxide, in order that they may raise the electronic conduction nature between a charge collector and an active material, electric conduction agents, such as graphite and acetylene black, are added in positive-electrode plied timber. Moreover, a binder is used, in order to paste up an active material, an electric conduction agent, and a charge collector and to produce an active material layer. On the other hand, compared with the aqueous intermediation system, these nonaqueous rechargeable battery had the high liquid viscosity of a solvent, and since conductivity was low, it had the fault that a low-temperature property and a load characteristic were inferior. Since high rate discharge is required also in the discharge last stage among the pocket devices which are the main applications of a nonaqueous rechargeable battery in a notebook computer or a video camcorder, especially amelioration of a load characteristic is an important problem.

[0004] The attempt of following many is made as a conventional technique for improving the load characteristic of a nonaqueous rechargeable battery. In respect of the cell design, cures, such as expansion-izing of an electrode surface product and porosity-izing of an electrode active material layer, are made. invention of JP,6-333558,A -- a positive electrode -- a mixture -- by using inner electric conduction material (carbon powder) as the mixture of graphite and amorphous carbon powder, the void content of a positive-electrode plate is adjusted and the load characteristic is improved.

[0005] However, since the content volume of a cell is fixed, on the other hand, such a cure will become constraint of the fill of the active material to an electrode, i.e., cell

capacity. Therefore, the amelioration by the side of ingredients, such as an electrode component, and the electrolytic solution, a separator, is also requested from load characteristic amelioration.

[0006] The attempt which the touch area of an active material front face and the electrolytic solution is increased by atomization, and improves a load characteristic is made also about positive active material. For example, in invention of JP,9-320603,A, the powdered active material obtained by heat-treating the solution made to emulsify an active material raw material in a flammable liquid after spraying baking is the secondary aggregate of the particle whose particle diameter is about 0.1 micrometers, and the charge-and-discharge property in high current density is improved.

[0007] However, if an active material is atomized in this way, the initial complement of electric conduction material or a binder will also increase, and the filling factor of the active material to a positive-electrode plate will be restrained. Moreover, the mechanical property of the paint film at the time of coating-izing will become weak firmly with atomization, and the problem of being easy to produce exfoliation of a paint film at the winding process at the time of cell assembly will also be produced. The technique of improving the restoration nature of the active material to a cell plate is indicated by JP,9-129230,A by using for positive active material the mixture of the minute crystal grain child whose unidirectional particle diameter in SEM observation is 0.1-2 micrometers, and the spherical aggregated particle whose unidirectional particle diameter in SEM observation is 2-20 micrometers. However, by such approach, since the consideration to osmosis / diffusion path of the electrolytic solution inside a spherical aggregated particle was not made, there was a problem that the load characteristic amelioration effectiveness by atomization of the diameter of a primary particle could not be discovered.

[0008]

[Problem(s) to be Solved by the Invention] As mentioned above, although amelioration of load characteristics, such as porosity-izing of the electrode active material layer in respect of a cell design and atomization of the positive active material itself, was tried, such a cure had technical problems, such as becoming constraint of the active material fill to an electrode, i.e., cell capacity, on the other hand. Therefore, the purpose of this invention is to offer the nonaqueous rechargeable battery which used them for the improvable positive active material and the positive-electrode list of a load characteristic, without spoiling the restoration nature of the active material to a positive electrode.

[0009]

[Means for Solving the Problem] this invention persons checked that it was effective to control the shape of particle of positive-active-material powder to a porous spherical aggregated particle, in order to reconcile the amelioration effectiveness of the load characteristic by atomization of a positive-active-material particle, and control of the increment in an initial complement of the electric conduction material and binder accompanying atomization about the above-mentioned technical problem, as a result of repeating examination wholeheartedly from the viewpoint of the structure of positive active material and a positive electrode.

[0010] By considering as porous structure, by optimizing the pitch diameter of the pore (opening pore) which the solid-liquid touch area of a detailed primary particle front face and the electrolytic solution becomes large, and carries out opening to a particle front face from the interior of a particle, migration diffusion of the electrolyte in pore is made

easy, and the increment in the internal resistance at the time of high charge and discharge can be controlled. Moreover, since a configuration is a spherical aggregated particle, the fluid improvement as fine particles and reduction of the slurry viscosity when coating-izing using an organic solvent are also expectable. Using the spherical aggregated particle of such porosity as positive active material, it mixes with carbon system electric conduction material and a binder, and a positive-electrode binder layer is formed in the shape of film on a charge collector. The obtained positive-electrode binder layer serves as the structure where the porosity spherical aggregated particle of positive active material was held in the arborescence network of carbon system electric conduction material. Therefore, the amount of electric conduction material required to form the network of the electric conduction material from a current collection body surface to each aggregated particle and the amount of a binder required to secure the binding reinforcement of a positive-electrode binder layer can be reduced, and the fill of the active material to a positive electrode can be improved as the result.

[0011] That is, this invention is Co, nickel, and Mn to the 1st. It is the particle of the porosity which consists of a lithium multiple oxide which uses as a principal component one or more sorts of elements chosen from a group, and a lithium. It is within the limits whose pore pitch diameter in the pore distribution measurement by the method of mercury penetration is 0.1-1 micrometer. Positive active material for nonaqueous rechargeable batteries characterized by the sum total of the volume of pore with the path of 0.01 to 1 micrometer consisting of a particle which is more than 0.01cm³/g; to the 2nd The positive electrode for nonaqueous rechargeable batteries characterized by using the positive active material of a publication for said 1st [the]; to the 3rd In the positive electrode with which positive active material is the lithium multiple oxide in which insertion and desorption are possible reversibly about a lithium ion, and the mixture of this positive active material, carbon system electric conduction material, and a binder was formed in the shape of film on the charge collector As a porous aggregated particle lump with which the above-mentioned positive active material is positive active material given in said 1st [the], and primary particles gathered The positive electrode for nonaqueous rechargeable batteries characterized by being held in the arborescence network of carbon system electric conduction material; the 4th is provided with the nonaqueous rechargeable battery characterized by using the positive active material of a publication said 1st [the].

[0012]

[Embodiment of the Invention] In the positive electrode with which the positive active material of the positive electrode for nonaqueous rechargeable batteries of this invention is the lithium multiple oxide in which insertion and desorption are possible reversibly about a lithium ion, and the mixture of this positive active material, carbon system electric conduction material, and a binder was formed in the shape of film on the charge collector The above-mentioned positive active material is a suitable positive electrode for the nonaqueous rechargeable battery which was characterized by being held in the arborescence network of carbon system electric conduction material as a porous aggregated particle lump with which primary particles gathered, and was excellent in the load characteristic. here, let one or more sorts of the transition elements and lithiums which are chosen from the group of Co, nickel, and Mn be principal components with a lithium multiple oxide -- stratified -- or -- pseudo--- the thing of stratified or an oxide

with Spinel structure is shown.

[0013] By setting up the structure of a positive electrode as mentioned above, even when the touch area of an active material and the electrolytic solution is enlarged, and activation polarization is reduced and the hyperviscous organic electrolytic solution is used, the path of the suitable electrolytic solution which can control concentration polarization can be secured. As the result, the nonaqueous rechargeable battery excellent in the load characteristic with few capacity falls is producible also in the time of high charge and discharge.

[0014] In order to produce such a positive electrode for nonaqueous rechargeable batteries, selection of an active material is important. That is, the sum total of the volume of pore with the path which the positive active material of this invention is a spherical aggregated particle which has the pore of opening nature which consists of a multiple oxide which uses as a principal component one or more kinds of transition elements chosen from the group of Co, nickel, and Mn and a lithium, and the pore pitch diameter in the pore distribution measurement by the method of mercury penetration is within the limits which is 0.1-1 micrometer, and is 0.01-1 micrometer is 0.01cm³/g. It be characterized by being above. As a measuring method of pore volume distribution, a method of mercury penetration and a gas adsorption-and-desorption method are typical, and the latter of the former is effective in measurement of several angstroms - dozens of nm minute pore to measurement of several nm - about hundreds of micrometers big pore size. This invention estimated using the method of mercury penetration (the : trade name pore master 60 made from can TAKUROMU (U.S.) was used for the measuring device). In addition, although a part for the opening between aggregated particles is also contained in the pore volume distribution measured with the method of mercury penetration, the pore pitch diameter of the active material powder in this invention is the value computed only about the internal pore of the aggregated particle except a part for this opening.

[0015] In this invention, when under this minimum of the amelioration effectiveness of a load characteristic is [specifying a pore pitch diameter in the range of 0.1-1 micrometer] insufficient and this upper limit is exceeded, it is to saturate the amelioration effectiveness of a load characteristic and for the evil of the tap density fall by internal pore being too large to arise. In addition, with a pore pitch diameter here, in order to except particle interspace spare time, it computes from the result of having measured pore distribution in 0.01 to 1 micrometer. Moreover, the sum total volume of the pore of the path of the above-mentioned range is specified for a load characteristic falling remarkably or more [0.01cm] to three at under this numeric value.

[0016] The mean particle diameter of the above-mentioned spherical aggregated particle is 4-20 micrometers, and tap density is 1.8g/cc or more, and the point of inflection of the rate of a volume decrease by the Cooper plotting method the positive active material of this invention It is still more desirable that it is 500kg/cm² or more. The reason is explained below. Since slurry viscosity goes up in case the fluidity as fine particles gets worse that the mean particle diameter of a spherical aggregated particle is less than 4 micrometers, or it mixes with an organic solvent and coating-izes, it is not desirable. Moreover, if mean particle diameter exceeds 20 micrometers, in order for the electronic conduction nature inside an aggregated particle to fall, a load characteristic will deteriorate.

[0017] In case it pressurizes and fabricates and the volume density of a positive electrode

is adjusted after mixing an active material, carbon system electric conduction material, and a binder as tap density is less than 1.8g/cc, a high pressurization load is needed and it becomes disadvantageous industrially. The pressurization load at the time of producing a positive electrode using the positive active material of this invention should just be 0.3 - 2 ton/cm² in the case where volume density of a positive electrode is carried out in 3g/cc. In addition, tap density the measuring method used by this invention JIS Z 2504 It is the based tap method and is the laser scattering-about method about particle size distribution. [0018] Moreover, in order to maintain the configuration of a porous spherical aggregated particle within the production process of a positive electrode, it is necessary to specify the cohesive force between the primary particles which constitute this aggregated particle. Especially when coating-izing positive-electrode plied timber and applying on a charge collector, an aggregated particle is easy to **** at the distributed process at the time of coating-izing, and there is a possibility that the improvement effect of a load characteristic may fall. Generally as an appraisal method of the state of aggregation of granularity fine particles, the Cooper (Cooper) plotting method which plots the rate of a volume decrease in the compression process of fine particles (**** of the following type) by the pressurization pressure (natural-logarithm graduation) is used.

[0019]

[Formula] $= a_1 \exp(-k_1 [(V_0 - VP) / (V_0 - VF)] / P + a_2 \exp(-k_2 / PP)$: Initial restoration volume VP of pressurization pressure (kg/cm²) V₀: (cm³) :P The restoration volume (cm³)

VF: closest-packing volume (cm³) constant at the time of kg/cm² pressurization: k₁, k₂, a₁, a₂ [0020] Thus, when the Cooper plot of the rate of a volume decrease in the

compression process of fine particles is carried out and linear regression cannot be carried out, the point of inflection where two straight lines cross may be shown. In this case, it means that floc was destroyed by pressurization and compression behavior changed. In this invention, in order to specify the reinforcement of a porosity aggregated particle, let point of inflection of the rate of a volume decrease when analyzing the rate of a volume decrease when compressing positive-active-material powder by the Cooper plotting method be an index. In addition, as a Measuring condition, the pressurization pressure range was made into 0 - 2.5 ton/cm², and VF in the above-mentioned formula computed the rate of a volume decrease as restoration volume in 2.5 ton/cm².

[0021] The point of inflection of the rate of a volume decrease by the above-mentioned Cooper plotting method If it is 500kg/cm² or more, destruction of a porosity aggregated particle will not arise in the usual positive-electrode production process. In addition, when the point of inflection of the rate of a volume decrease is not measured clearly, it is 500kg/cm² or more. The pressurized Plastic solid is broken and it is the fracture surface. It is good, if a SEM image is observed and destruction of an aggregated particle has not arisen. Moreover, the spherical aggregated particle of the porosity in this invention has the opening pore of a large number penetrated inside from a spherical aggregated particle front face, and is [the path of the opening pore] usually for a scale factor. The magnitude of extent which may be enough observed with a SEM photograph, i.e., the path of opening pore, A particle which is 5nm or more is shown.

[0022] Below, the manufacturing method of the spherical aggregated particle of the porosity in this invention is explained. Although the ellipsoid-like aggregated particle is indicated, such a particle carries out mixed baking of the spherical hydroxide which was similar with the aggregated particle of this invention and with which spherical or the

tabular primary particles which neutralized the sulfate with alkali and were obtained gathered with lithium salt, and is obtained by JP,7-37576,A. It is the pore pitch diameter of the baking object generally obtained in the hydroxide obtained using a sulfate in order tap density is high, and sintering between the primary particles at the time of baking is controlled by existence of the sulfuric-acid root which mean particle diameter is about 1-5nm, and remains in a hydroxide at a minute amount and to hold the skeleton of the hydroxide which is a start raw material. It is set to 5nm or less. However, also in such an approach, preparation of the positive-active-material powder of this invention is possible by controlling the solution temperature at the time of neutralizing especially a sulfate, pH, liquid Nakashio concentration, a neutralization rate, etc.

[0023] That is, by controlling the solution temperature at the time of neutralizing a sulfate, pH, liquid Nakashio concentration, a neutralization rate, etc., tap density is comparatively low, and it has the pitch diameter of 0.1-1 micrometers or more, and the sum total volume of pore is 0.01cm³/g. The above hydroxide can be prepared. Moreover, it becomes possible to prepare the positive-active-material powder which improves tap density by sintering and has the description which was described above, leaving pore by carrying out mixed baking of this with lithium salt. Moreover, preparation of positive-active-material powder with the description which described above the mixture of each compound of a transition element and a lithium other than such an approach also by the approach of coming direct or the thing which carried out temporary quenching, and carrying out actual baking is possible. It is at 500-800 degrees C about the mixture of each compound of the concrete approach, one or more sorts of transition elements chosen from the group of Mn, Co, and nickel as one, and a lithium. Temporary quenching is carried out for 5 to 20 hours. Subsequently, it is at the temperature of 900 degrees C or less more highly [spray and corn the baking object which carried out temporary quenching after **** distribution, and] 30 degrees C or more than temporary-quenching temperature. A porous spherical aggregated particle can be manufactured by carrying out actual baking for 1 to 5 hours.

[0024] The positive electrode for nonaqueous rechargeable batteries which consists of positive active material which consists of the above-mentioned porosity spherical aggregated particle can be manufactured by the following approach. That charge collector is aluminium foil and, as for this positive electrode, the above-mentioned porosity spherical aggregated particle is held as an active material at it. After such a positive electrode mixes 3 - 6 % of the weight of polyvinylidene fluorides which are a binder, and 3 - 9 % of the weight of carbon which is an electric conduction agent with 85 - 94 % of the weight of positive active material of the above-mentioned porosity aggregated particle in the case of a wet method, adds suitably N-methyl pyrrolidone (NMP) which is a solvent and prepares it in the shape of a paste, it is applied, dried and pressed in both sides of a charge collector ingredient, and is manufactured to them. Moreover, in the case of dry process, the obtained moldings is rolled out and manufactured after kneading and fabricating 3 - 6 % of the weight (PTFE) of polytetrafluoroethylenes which are a binder, and 3 - 9 % of the weight of carbon which is an electric conduction agent with 85 - 94 % of the weight of positive active material of the above-mentioned porosity spherical aggregated particle.

[0025] In addition to the above-mentioned positive electrode, evaluation of the cell property of the above-mentioned positive active material is performed to a negative

electrode by using the film of polypropylene for a separator for a metal lithium. What dissolved LiPF₆ in the liquid which mixed ethylene carbonate and carbonic acid diethylene to 1:1 by the volume ratio by the concentration of 1 mol/dm³ as an electrolyte is used for the electrolytic solution. Charge and discharge are performed with the current density of 0.5 mA/cm², charge to 4.3V, discharge to after that 2.7V, and are taken as the discharge capacity per unit weight of positive active material. A load characteristic performs discharge by current density 5.0 mA/cm² and 10 mA/cm², respectively, after charging by current density 0.5 mA/cm². The index of evaluation is capacity retention about the discharge capacity in each current density at the time of making discharge capacity when discharging by current density 0.5 mA/cm² into 100%. It may be (%). Hereafter, although explained to a detail with an example, the range of this invention is not limited by these.

[0026]

[Example 1] The mole ratio of each metal carried out preferential grinding of a lithium hydroxide, nickel hydroxide, and the cobalt hydroxide with the ball mill at a rate of 105:90:10, pressing of the obtained mixed powder was carried out under the pressure of 1 ton/cm², and this molding object was used as the raw material for baking. This raw material was calcinated in the air air current at 770 degrees C for 10 hours (temporary quenching). After making the obtained baking object suspend so that it may become 40% of the weight of concentration to pure water, it added and surface treatment of a nitric acid and the lithium nitrate was carried out so that the particle after this baking of a back process might become porosity, **** grinding was carried out with the wet bead mill for 2 hours, and desiccation granulation was spherically carried out by the spray drying method. this granulation powder -- 800 degrees C -- the inside of 2 hours and an oxygen air current -- baking (this baking) -- carrying out -- a mortar -- after ****(ing) with type disintegrator, the particle size regulation was carried out with the screen classifier. Thus, the obtained lithium multiple oxide was the spherical aggregated particle of the porosity whose sum total volume of pore with the pore pitch diameter of 0.363 micrometers and a 0.01-1-micrometer diameter is $8.4 \times 10^{-2} \text{ cm}^3/\text{g}$. Although the positive-electrode plate was produced using the lithium multiple oxide of this example 1 as positive active material and being pressed by the pressure of 750kg/cm², the porosity spherical aggregated particle was not destroyed but sufficient load characteristic was acquired.

[0027]

[Example 2] To the example 1, conditions were changed into 650 degrees C and temporary-quenching temperature was performed at them. The crystallinity of a primary particle was reduced by lowering temporary-quenching temperature compared with an example 1, sintering between primary particles was promoted, and pore volume was controlled. Thus, the obtained lithium multiple oxide was the spherical aggregated particle of the porosity whose sum total volume of pore with the pore pitch diameter of 0.137 micrometers and a 0.01-1-micrometer diameter is $1.8 \times 10^{-2} \text{ cm}^3/\text{g}$.

[0028]

[The example 1 of a comparison] Nickel hydroxide and cobalt hydroxide were performed to the example 1 using what neutralized each sulfate and was prepared. Thus, the obtained positive active material was the spherical aggregated particle of the porosity whose sum total volume of pore with the pore pitch diameter of 0.053 micrometers and a 0.01-1-micrometer diameter is $1.8 \times 10^{-3} \text{ cm}^3/\text{g}$.

[0029]

[The example 2 of a comparison] **** distribution time amount in a wet bead mill was performed over 4 hours to the example 1. the crystallinity of a primary particle is fallen by lengthening **** distribution time amount compared with an example 1 -- making -- in addition -- and by what a front face is activated for (amorphous-izing), sintering between primary particles was promoted and pore volume was controlled small intentionally. Thus, the obtained positive active material advanced and its sintering of a primary particle was the spherical aggregated particle of the porosity whose sum total volume of pore with the pore pitch diameter of 0.211 micrometers and the path which is 0.01-1 micrometer is $5.0 \times 10^{-3} \text{ cm}^3/\text{g}$.

[0030]

[The example 3 of a comparison] It is a carrying-out [to the water solution which made temporary-quenching powder suspend / by adding a superfluous nitric acid and a superfluous lithium nitrate (twice in the case of an example 1) / further]-to example 1- surface treatment thing. By adding many nitric acids and lithium nitrates compared with an example 1, sintering between primary particles was promoted and pore volume was controlled small intentionally. Thus, the volume of pore with the pore pitch diameter of 0.300 micrometers and a 0.01-1-micrometer diameter was $1.6 \times 10^{-3} \text{ cm}^3/\text{g}$, and the obtained positive active material was the spherical aggregated particle to which sintering progressed.

[0031]

[The example 4 of a comparison] The mole ratio of each metal carried out grinding mixing of a lithium hydroxide, nickel hydroxide, and the cobalt hydroxide with the ball mill at a rate of 105:90:10, pressing of the obtained mixed powder was carried out under the pressure of 1 ton/cm², and this molding object was used as the raw material for baking. This raw material was calcinated in the air air current at 770 degrees C for 10 hours. this baking powder -- a mortar -- after ****(ing) with type disintegrator, the particle size regulation was carried out with the screen classifier. Thus, the volume of pore with the pore pitch diameter of 0.085 micrometers and a 0.01-1-micrometer diameter was $3.2 \times 10^{-3} \text{ cm}^3/\text{g}$, and the obtained positive active material was the aggregated particle of the form which the primary particle condensed.

[0032]

[The example 5 of a comparison] It is [cobalt hydroxide / a lithium hydroxide, nickel hydroxide, and] the **** distribution time amount in 800 degrees C and a wet bead mill about temporary-quenching temperature to 105:87:13 in the mole ratio of each metal to an example 1. Whenever [glost firing Nariatsu] was made into 830 degrees C, and was performed for 30 minutes. an example 1 -- comparing -- temporary-quenching temperature -- high -- in addition -- and by shortening **** distribution time amount, the diameter of a primary particle was large and prepared intentionally the aggregated particle of the condition that apparent density gravity is low. Thus, the obtained positive active material was the spherical aggregated particle of the porosity which consisted of primary particles to which sintering is not progressing. As for the porosity aggregated particle, it was observed that destruction is progressing, although the positive-electrode plate was produced based on the positive active material of the example 5 of a comparison and being pressed by the pressure of 750kg/cm². The measurement result and load characteristic of pore distribution of examples 1-2 and the example 1-4 of a

comparison are shown in Table 1. Only when the volume of the pore which is in within the limits whose pore pitch diameter is 0.1 micrometers - 1 micrometer from this table, and has a 0.01 micrometers - 1 micrometer diameter is three or more active material unit weight (1g) per 0.01 cm, a high load characteristic is shown and it turns out except it that a load characteristic is inferior. Moreover, the point of inflection of the mean particle diameter of examples 1-2 and the example 5 of a comparison, tap density, and the rate of a volume decrease by the Cooper plotting method is shown in Table 2. the case of this table to the examples 1-2 -- tap density -- three or more 1.8 g/cm -- it is -- in addition -- and it turns out that the point of inflection of the rate of a volume decrease of the Cooper plot shows a high load characteristic compared with the example 5 of a comparison which both are 500kg/cm² or more and is below the above-mentioned numeric value.

[0033]

[Table 1]

実施例 1～2 と比較例 1～4 の細孔分布測定および負荷特性測定結果

	均細孔径 (μm)	細孔容積 (cm^3/g)*	負荷特性(容量保持率(%))	
			5mA/cm ² 放電	10mA/cm ² 放電
実施例 1	0.363	8.4×10^{-2}	97.1	79.1
実施例 2	0.137	1.8×10^{-2}	95.6	79.9
比較例 1	0.053	1.8×10^{-3}	91.1	65.2
比較例 2	0.211	5.0×10^{-3}	89.5	68.4
比較例 3	0.300	1.6×10^{-3}	92.3	67.1
比較例 4	0.085	3.2×10^{-3}	95.8	66.5

* The pore volume of 0.01 micrometers - 1 micrometer of pore size per active material unit weight is shown.

[0034]

[Table 2]

実施例 1～2 と比較例 5 の平均粒径、タップ密度、クーパープロット法による

体積

減少率の変極点

	平均 粒径 (μm)	タップ 密度 (g/cm^3)	体積減少率の 変曲点 (kg/cm^2)	負荷特性 (容量保持率(%))	
				5mA/cm ² 放電	10mA/cm ² 放電
実施例 1	10.1	1.88	730	97.1	79.1
実施例 2	9.72	2.15	1500	95.6	79.9
比較例 5	12.1	1.35	310	91.2	69.9

[0035] Drawing 1 is the Cooper plot showing the rate of a volume decrease in the compression process of the positive active material obtained in examples 1 and 2 and the example 5 of a comparison, and point of inflection It is 730kg/cm² to which it exceeds 500kg/cm² to the case of the example 5 of a comparison which does not amount to 500kg/cm² in the case of an example 1, and the point of inflection where an example 2 is not illustrated is 1500kg/cm².

[0036]

[Effect of the Invention] As stated above, it sets to the positive electrode for nonaqueous rechargeable batteries of this invention. Positive active material Li ion by within the limits whose pore pitch diameter in the pore distribution measurement by the method of mercury penetration it is the aggregated particle of the porosity to which the primary particles reversibly prepared from Li multiple oxide in which insertion and desorption are possible gathered, and is 0.1-1 micrometer The sum total volume of pore with a 0.01-1-micrometer diameter is more than 0.01cm³/g, and mean particle diameter especially as a spherical aggregated particle It is 1.8g/cc or more in 4-20 micrometers and tap density. And since the point of inflection of the rate of a volume decrease by the Cooper plotting method has the property of 500kg/cm² or more The mixture of the above-mentioned positive active material, a carbon system electric conduction agent, and a binder is suitable for the nonaqueous rechargeable battery which excelled [time / of high charge and discharge] in the load characteristic with few capacity falls as a positive electrode formed in the shape of film in the shape of a charge collector.

